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Measurement of Non-Linear Optical Absorption of PVC/TiO₂ Nanocomposite via Z-Scan Technique for Optical Limiting

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Abstract: This research focuses on PVC/TiO₂ nanocomposites in the form of thin films in order to expand our understanding of photonics technology. For fabrication of the thin films, the casting method was used with nanocomposites composite were developed by mixing TiO₂ nanoparticles with Polyvinyl Chloride (PVC) as the polymer matrix. The absorbance parameters were determined using spectral analysis, and the linear absorption coefficient was computed. A single beam Z-scan technique was used to evaluate the nonlinear refractive index and nonlinear absorption coefficient via a CW diode pumped solid state (DPSS) laser (Coherent Verdi-V5, 532 nm) was employed as the excitation laser at 50mW. Peak absorption was detected at 280 nm with increasing absorption observed as the proportion of TiO₂ nanoparticles increased. The nonlinear absorption coefficient was found at (0.5342, 1.3585, 1.5999, and 0.0253) 1×10^{-5} cm/W. All of the sample morphology resulting poor structure which then affect the NLO absorption of the materials. However, with the positive value of NLO absorption, they appear to be promising candidates for optical limiting applications.

Keywords: NLO; Absorption; PVC/TiO₂, Casting Method, Z-Scan

I. INTRODUCTION

Nonlinear optics (NLO) is a fascinating branch of physics that investigates the subtle interaction of light and matter that extend beyond the limits of linear optics. Over the years, researchers have discovered a wealth of nonlinear optical phenomena, such as sum and difference frequency creation, dynamic amplification, and four-wave mixing [1]. Each finding added to our understanding of light-matter interactions and creating opportunities of optical phenomena to investigate. Another area of study is the development of new nonlinear optical devices and components. Efforts are being made to design and manufacture compact and efficient nonlinear optical devices such as frequency converters, optical switches, and optical limiting [2]. These developments are intended to improve the operation of existing optical systems while also setting the way for future advances in technology. On the other hand, polymer materials have come to be as flexible and potential nonlinear optics (NLO) choices. Polymer material development has made significant progress in recent years. It offers various interesting qualities, including low cost, simplicity of production, flexibility, and tunability of properties [2]. These features make polymers highly desirable for a variety of applications, including optics and photonics. Furthermore, doping polymers with suitable substances improves their nonlinear optical characteristics even further [3]. Doping can change the refractive index, increase nonlinear susceptibility, and improve polymer matrix stability [2,4].

As be mentioned before, NLO has been reinvented by nanoparticle materials, which provide remarkable manipulation of light-matter interactions at the nanoscale. Nanoparticles act as doping agents in NLO materials, improving their nonlinear optical characteristics [5]. One can control the properties and responses of the composite material by including nanoparticles into host materials. This process results in increased nonlinear effects, such as higher nonlinear susceptibility and improved optical response [5]. Thus, the use of nanoparticles as doping agents into polymer matrices has proven useful in modifying and improving the nonlinear optical characteristics of composite materials which would benefits NLO application such as optical limiting and optical switching.

II. MATERIALS AND METHODS

To begin, the 80mg of PVC supply by Sigma-Aldrich were added in 1.0 mL of tetrahydrofuran (THF). The magnetic stirrer with angular velocity of 400 rpm and timed for one hour at room temperature was used to help dissolve and prevent agglomerates. The PVC/THF solution was deduce a neat clear solution. Second, the titanium dioxide (TiO₂) acquired also from Sigma-Aldrich. Nanoparticles (size 13 nm) in varied quantities (0, 5, 10, and 15) wt% were introduced slowly to a PVC/THF combination. The solution then, undergo stirrer process with the same set up for 2 hours until it achieved a satisfy homogenous solution.

Lastly, the solution was poured consistently on a glass petri dish and leave the sample one day at room temperature for it to dry. After a day, the film was readily removed and the thin film of pure PVC and nanocomposites (PVC/TiO₂) of varying concentrations were obtained.

The morphology of the samples was studied using scanning electron microscopy (SEM) brand JSM-5510LV, JEOL. The samples were set up inside the SEM chamber and exposed to a focus electron beam voltage of 5kV at 500 μ m. ImageJ analysis software was also used to determine the thickness of the samples [6]. The linear transmittance spectra of the samples were also examined with a UV-VIS-NIR spectrophotometer from SHIMADZU CORP UV-3600 Plus . A CW diode pumped solid state (DPSS) laser (Coherent Verdi-V5, 532 nm) was employed as the excitation laser at 50mW. Two silicon amplified photodetectors (PDA55, Thorlabs) were used in the setup. The material sample was first placed at the focal plane of a lens system and was mounted into a precision motorized stage (LTS-300, Thorlabs) with jog step of 300 mm. The sample was then scanned along the axial direction with a focused laser beam. The focused laser was split by a 50:50 beam splitter after passed through the samples and were detected by both detectors. One of the pair of photodetectors was positioned after an aperture or closed z-scan which will be used to study the mechanisms that result in nonlinear refraction, whereas the other was positioned in front of a lens or open z-scan which will be sensitive to the nonlinear absorption reaction. Both of information was recorded by oscilloscope.

III. RESULTS AND DISCUSSION

In this study, the morphology observation for PVC/TiO₂ of different concentration are retrieved. SEM images of all four PVC/TiO₂ nanocomposites via SEM machine at a voltage of 5 kV. SEM micrographs of PVT0, PVT5, PVT10, and PVT15 samples at a 500 μ m scale are shows in Figure 5. Visual observation demonstrates that pure PVC thin film and PVC/TiO₂ thin films with (5,10, 15) wt% concentration shows higher surface roughness. Based on PVT5, PVT10 and PVT15, the nanofillers are seem dispersed unequally in the host material. A rise in surface roughness could suggest a change in the material's morphology and a smooth and uniform surface, as in thin films is much more desirable for achieving maximum transmission and reflection of material towards [6] light which later would affect the NLO absorption response.

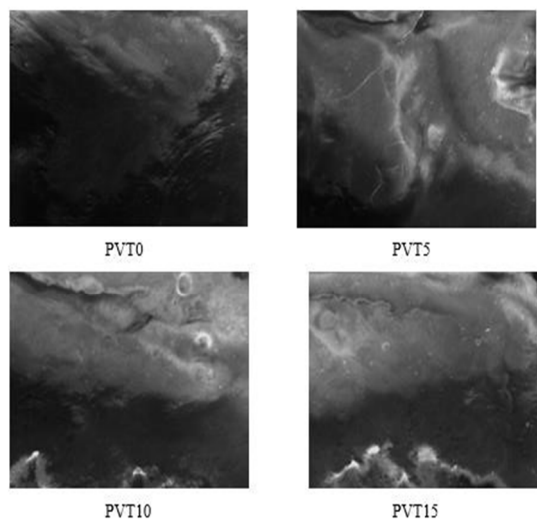


Figure 5: A compilation of SEM image of the samples PVT0 for pure PVC, PVT5 for PVC/TiO₂ (5wt%), PVT10 for PVC/TiO₂ (5wt%) and PVT 15 FORPVC/TiO₂ (5wt%)

The UV-visible absorption spectrum of PVC and PVC/TiO₂ nanocomposites as thin films are shown in Figure 6. The absorbance of pure PVC is low in both the UV and visible regions, whereas the absorbance of PVC/TiO₂ nanocomposites is high in the UV area, displaying that the absorption peak at 280 nm is due to the behaviour of TiO₂ nanoparticles. This indicates it can absorb light in the UVA range (280- 350) nm. However, the sample for concentration of 15wt% shows lower peak absorption than the dopped concentrations of 5wt% and 10wt%. due to very poor of surface structure.

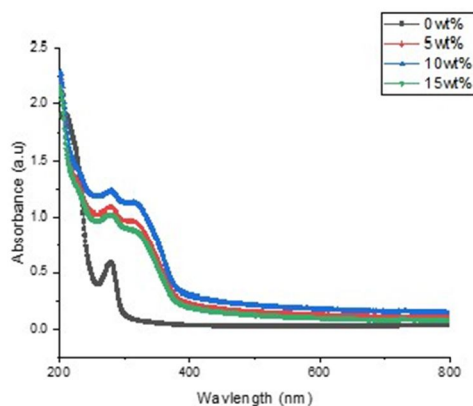


Figure 6: Absorption spectrum of PVC/TiO₂ nanocomposites as thin film.

Figure 7 demonstrate the linear absorption coefficient spectrum of pure PVC and PVC/TiO₂ nanocomposites as thin films, which fluctuate based on the wavelength of light absorbed. The absorption coefficient values for thin film samples were significantly differ due to the inversely proportional to the thickness of the sample. The thin film samples showed little differ for both the value of between UV and visible region. All samples are showed a reduction in the value of with increasing wavelengths, however with the grew amount of TiO₂ nanoparticles in the nanocomposites , particularly at short wavelengths.

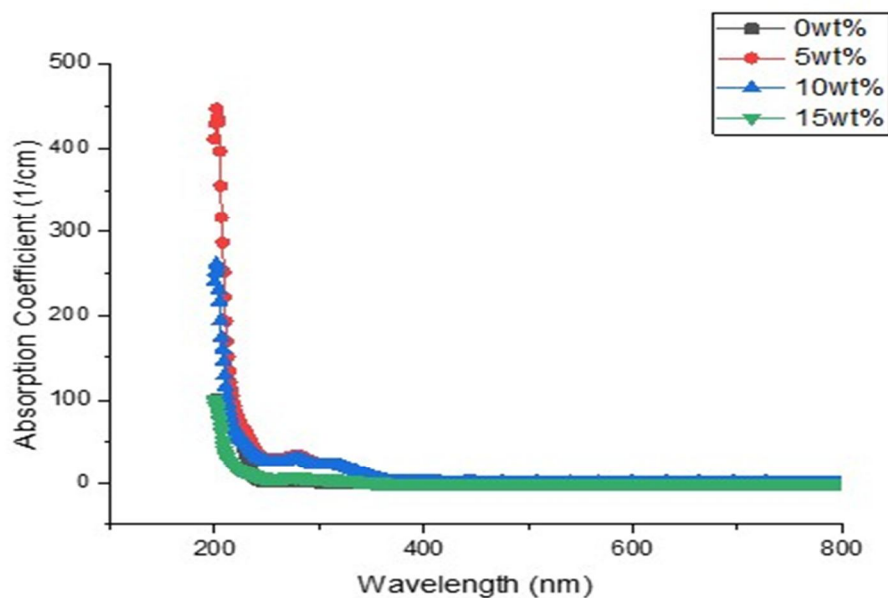


Figure 7: Linear absorption coefficient of PVC/TiO₂ nanocomposites as thin film.

The beam's radius at the focus was determined to be 36 μ m and Rayleigh length was calculated using equation 3.6.2 and it is 8.982 mm. It bigger than the sample thickness, which is a crucial requirement for the Z-scan approach [2,5]. The significant nonlinear effect in this study was attributed to TiO₂ nanoparticles. When examined using the same approach, the pure PVC displayed a barely nonlinear optical response at 532 nm.

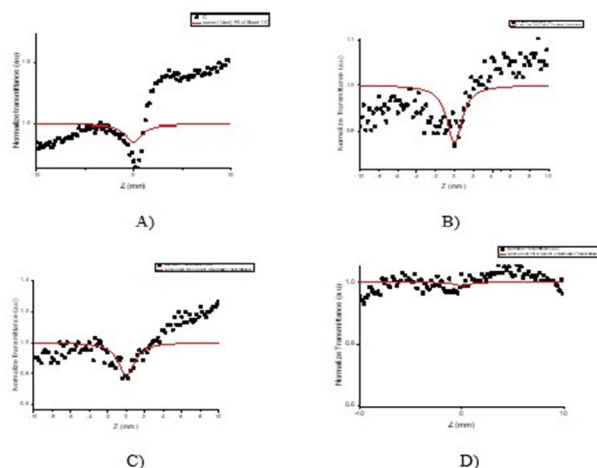


Figure 8: The compilation graph of normalize transmittance against Z. A for pure PVC, B for PVC/TiO2 5wt%, C for PVC/TiO2 10wt% and D for PVC/TiO2 15wt%

Based on Figure 9, the valley with the highest concentration of TiO2 nanoparticles was deeper than the valley with the lowest concentration in the samples. This suggests that nonlinear absorption is higher at high concentrations than at low concentrations. However, in the case of PVC/TiO2 15wt%, the supposedly result could not be obtained due to the poor structure fabrication which affects the transmittance and absorption of the laser. The nonlinear absorption coefficient is determined using equation 3.6.1, where Δt is the single valley value acquired from the open Z-scan data collected. Table 2 shows the values of $\Delta \phi_0$, L_{eff} , and β of PVC/TiO2 nanocomposites as thin films. The values of these parameters differed among nanocomposites samples are due to their absorption coefficient and the thickness of the sample, which varies between each other.

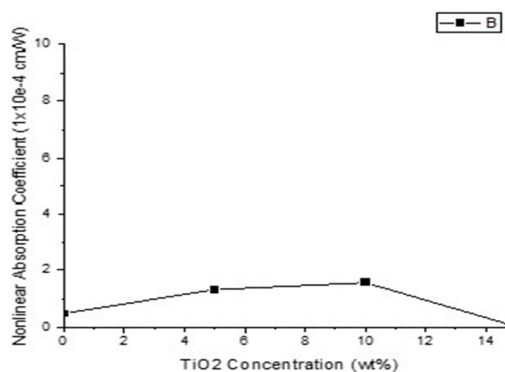


Figure 9 : Graph of Nonlinear absorption coefficient against TiO2 concentration

Samples	PVC/TiO2 0wt%	PVC/TiO2 5wt%	PVC/TiO2 10wt%	PVC/TiO2 15wt%
L_{eff} (1×10^{-3}) cm	8.9502	3.0534	5.1444	1.2274
β (1×10^{-5}) cm/W	0.5342	1.3585	1.5999	0.0253
$\Delta \phi_0$	2.4359	0.6263	1.3784	0.3899

Table 2: The list of samples measurement via Z-Scan Techniques

IV. CONCLUSION

The current study proposes a investigation framework for PVC/TiO₂ nanocomposite by studied and measuring upon nonlinear absorption properties. The prepared samples unfortunately did not met the basic requirements for thin film surfaces. However, the data retrieved still be important to study upon the affect morphology structure toward laser. The current work has also demonstrated of using Z Scan Technique in obtained the NLO properties. The technique approach yielded results that were quite similar to those obtained by others researcher. The PVC/TiO₂ can be consider as good candidate for optical limiting due to the positive values of nonlinear absorption.

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